

Surface diffusion coefficient near first-order phase transitions at low temperatures

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Abstract

We analyze the collective surface diffusion coefficient, D_c , near first-order phase transitions at which two low temperature phases coexist, using a lattice-gas model on a triangular lattice. Assuming the local equilibrium approximation, we obtain, both numerically and analytically, the dependence of D_c on the coverage and system size near such transitions. Four specific examples of transitions are considered for illustration. It is pointed out that the derived results are in fact rather general and not restricted only to the studied model.

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I. INTRODUCTION

The collective (or chemical) surface diffusion coefficient, D_c , is defined via the Fick's first law and represents a relevant transport coefficient for surface diffusion. Theoretical studies of D_c and of the influence of lateral interparticle interactions on D_c have employed various approaches, such as the mean-field, real-space renormalization group, and computer simulation techniques [1, 2]. One of the intriguing problems that has attracted particular attention is the effect of a phase transition on surface diffusion. Since lattice-gas models can be used to model the transition, they have provided a convenient framework in this regard [3–14]. However, below critical temperatures ordered phases may arise due to lateral interactions, and sophisticated arguments should be applied to analyze surface diffusion [6].

In this paper we investigate the coverage dependence of the diffusion coefficient D_c at low temperatures for a model on a regular triangular lattice in which phase transitions between ordered phases occur. To this end, we consider an approximate expression for D_c valid in the local equilibrium limit [6, 7],

$$D_c \approx D_c^0 e^{\beta\mu} \frac{P}{\chi/\beta}, \quad (1)$$

and use that the quantities in this expression can be obtained from the model finite-size free energy, f , that we derived in a previous paper [15] (here D_c^0 is the diffusion coefficient of non-interacting particles, $\beta = 1/k_B T$ is the inverse temperature, μ is the chemical potential, and χ is the isothermal susceptibility). In the approximation of Eq. (1) particles are assumed to migrate on the surface by jumps only to nearest-neighbor sites without any correlation between the jumps.

Several forms have been introduced for the configuration factor P . Nevertheless, many of them have an identical structure: they can be written as a sum of derivatives of f [6, 16, 17]. Therefore, we shall consider a very simple case in which P is identified with the probability that a lattice bond is vacant; then, on the triangular lattice, one has [6, 7]

$$P = 1 - 2\theta + \frac{1}{3}\xi, \quad (2)$$

where θ is the surface coverage and ξ is the statistical average number of occupied bonds per site. We will eventually show that our results do not pertain only to form (2) but are in fact general and can be readily extended to other forms of P .

The paper has the following structure. The studied model is introduced and its low temperature phases and free energy f are described in Sec. II. The coverage dependence of D_c is analyzed in Sec. III, focusing on the derivation of finite-size formulas for the dependence. Extensions of the obtained results to the more general forms of P are described in a final section.

II. THE MODEL

We assume that particles can be adsorbed on a solid surface only at sites forming a regular triangular lattice. The system contains a rectangular array with a large but finite number, N , of adsorption sites. Periodic boundary conditions are applied so that the array forms a finite torus whose cell is given, for example, by the vectors $(3n, 0)$ and $(0, 2\sqrt{3}n)$ with $n = 1, 2, \dots$ [the elementary lattice vectors are $(1, 0)$ and $(1/2, \sqrt{3}/2)$]; thus, $N = (3n) \times (4n)$. Each lattice site is either vacant or occupied by a particle. The model Hamiltonian is [6, 7]

$$H = \varepsilon_b N_b + \varepsilon_t N_t - \mu N_s, \quad (3)$$

where N_b , N_t , and N_s is the number of occupied bonds, elementary triangles, and sites, respectively, and ε_b and ε_t are bond and triangle interaction energies. This model was already used to study surface diffusion on a triangular lattice at high temperatures for the special cases when $\varepsilon_b = 0$ (with $\beta|\varepsilon_t|$ below 4.8) and $\varepsilon_t = 0$ (with $\beta|\varepsilon_b|$ below 10) [6, 7]. Here we consider the general case when both the bond and triangle interactions ε_b and ε_t are present and temperatures are sufficiently low.

As we proved in Ref. 15, model (3) has four ground states [see Fig. 1(a)]: a fully vacant state, σ_0 , a fully occupied state, σ_1 , and two threefold degenerate states, $\sigma_{1/3}$ and $\sigma_{2/3}$, with the partial coverages of $1/3$ and $2/3$, respectively. The ground-state diagram is shown in Fig. 1(b)–(d) and can be easily constructed by comparing the ground-state energies $e_0 = 0$, $e_1 = 3\varepsilon_b + 2\varepsilon_t - \mu$, $e_{1/3} = -\mu/3$, and $e_{2/3} = \varepsilon_b - 2\mu/3$. On the lines separating the ground-state regions of σ_0 and σ_1 , σ_0 and $\sigma_{2/3}$, and σ_1 and $\sigma_{1/3}$ only the two associated ground states coexist, while on the remaining lines (as well as at the points where three or all four ground-state regions meet) there is an infinite number of ground states, yielding in fact a residual entropy. Each ground state σ_α , $\alpha = 0, 1/3, 2/3, 1$, gives rise to a unique low-temperature phase, p_α , whose typical configuration looks as a ‘sea’ of the ground state σ_α with isolated

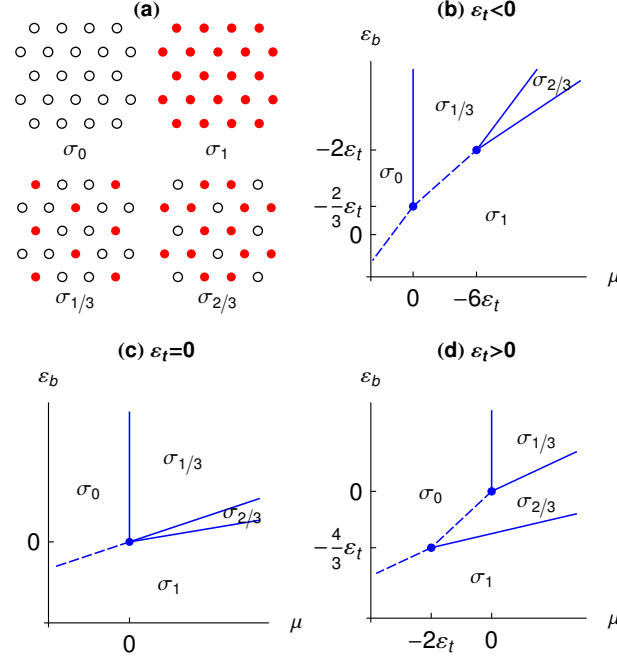


FIG. 1: (a) The ground states of the model. Circles (disks) represent (occupied) sites. (b)–(d) The ground-state diagram in dependence on the sign (attractivity or repulsivity) of the triangle interaction ε_t . Solid lines and disks correspond to those parts where infinitely many ground states exist, while dashed lines to the parts with a finite number of ground states.

‘islands’ of non-ground-state configurations, thus resembling the structure of σ_α . So, phase p_0 (p_1) is fully vacant (fully occupied), while phase $p_{1/3}$ ($p_{2/3}$) has the occupancy of $1/3$ ($2/3$). This holds only if the number of ground states remains finite, i.e., within each ground-state region and on the lines where only two ground states coexist. Consequently, a first-order phase transition can take place only between phases p_0 and p_1 , p_0 and $p_{2/3}$, and $p_{1/3}$ and p_1 .

Let us consider one of these pairs of phases to be denoted as p_- and p_+ (specific pairs of phases will be considered in Sec. III when applying the results to examples); the associated ground states are σ_- and σ_+ , respectively. At low temperatures and near the transition point μ_t (for $|\mu - \mu_t| \leq \text{const} / \beta \sqrt{N}$), the finite-size partition function, Z , can be expressed as a sum of two single-phase partition functions. Each of them contains only the contributions from the ground state σ_- or σ_+ and its thermal perturbations (the latter can be written in the form of a cluster expansion). As a result, the finite-size specific free energy, $f = -(1/\beta N) \ln Z$, reads [15, 18]

$$f(\mu) = -\frac{1}{\beta N} \ln[\nu_- e^{-\beta f_-(\mu)N} + \nu_+ e^{-\beta f_+(\mu)N}] + r, \quad (4)$$

where the degeneracy ν_{\pm} of phase p_{\pm} is $\nu_0 = \nu_1 = 1$ and $\nu_{1/3} = \nu_{2/3} = 3$ and the error $r = O[\exp(-\text{const } \beta \sqrt{N})]$ [the symbol $O(x)$ is used to denote a term that can be bounded by $\text{const } x$]. Moreover, the single-phase specific free energies f_{\pm} are essentially equal to the specific energies, e_{\pm} , of ground state σ_{\pm} because the contributions from the thermal perturbations of σ_{\pm} are exponentially suppressed in β (the Peierls condition). Taking into account only one-site perturbations (which represent the leading corrections), one has [15]

$$f_{\alpha} \approx e_{\alpha} - \frac{1}{\beta} \ln[(1 + e^{-\beta \Delta H_{\alpha}^{\circ}})^{\alpha} (1 + e^{-\beta \Delta H_{\alpha}^{\bullet}})^{1-\alpha}], \quad (5)$$

where

$$\begin{aligned} \Delta H_0^{\bullet} &= -\Delta H_{1/3}^{\circ} = -\mu, \\ \Delta H_{1/3}^{\bullet} &= -\Delta H_{2/3}^{\circ} = 3\varepsilon_b - \mu, \\ \Delta H_{2/3}^{\bullet} &= -\Delta H_1^{\circ} = 6\varepsilon_b + 6\varepsilon_t - \mu \end{aligned} \quad (6)$$

are the energy excesses of one-site perturbations of σ_{α} over the energy of σ_{α} (the superscript ‘o’ corresponds to removing one particle from σ_{α} and ‘•’ to adding one particle to σ_{α}). Since a particle can be only added to σ_0 (removed from σ_1), in Eq. (5) for f_0 (f_1) the first (second) term in \ln is set equal to 1.

The free energy f of the model can be readily evaluated from Eqs. (4) and (5). In addition, the transition point μ_t can be also obtained—it is the solution of the equation $f_-(\mu_t) = f_+(\mu_t)$ [18].

III. THE COVERAGE DEPENDENCE OF D_c

Relations (1) and (2) allows one to calculate an approximate value of the diffusion coefficient D_c in the local equilibrium limit from the free energy f . Indeed, it suffices to find the derivatives

$$\theta = -\frac{\partial f}{\partial \mu}, \quad \chi = -\frac{\partial^2 f}{\partial \mu^2}, \quad \xi = \frac{\langle N_b \rangle}{N} = \frac{\partial f}{\partial \varepsilon_b}. \quad (7)$$

Hence, in combination with Eq. (4) that holds analogously also for derivatives of f [18], the dependence of D_c on μ immediately follows. Consequently, the coverage dependence of D_c follows upon obtaining the inverse to $\theta(\mu)$ and substituting it into $D_c(\mu)$, which can be easily carried out numerically.

However, we can also derive explicit finite-size formulas for $D_c(\theta)$, starting from the μ dependences of θ , ξ , and χ as yielded by Eqs. (4) and (7). Without loss of generality, we

will assume that phase p_- (p_+) is stable for μ below (above) μ_t . Then the coverage jump at the transition is $\Delta\theta = \theta_+ - \theta_- > 0$, where θ_{\pm} are the single-phase coverages, $-\partial f_{\pm}(\mu)/\partial\mu$, at μ_t .

Notation. As a rule, we use Δq to denote the difference, $q_+ - q_-$, of single-phase quantities q_+ and q_- .

It turns out that three regimes may be distinguished according to the relative importance of phase p_- and p_+ as given by the weights

$$\lambda_{\pm}(\mu) = \frac{1}{1 + \rho^{\pm 1} e^{\pm \beta \Delta f(\mu) N}}, \quad (8)$$

where the ratio $\rho = \nu_-/\nu_+$. Note that $0 < \lambda_{\pm} < 1$ and $\lambda_- + \lambda_+ = 1$. In addition, since the stable phase has the lowest specific free energy, for μ below (above) μ_t the difference Δf is positive (negative) and the weight λ_- (λ_+) approaches 1 exponentially fast. At μ_t the specific free energies are identical, and the two weights are equal to 1/2 if $\rho = 1$ and to 1/4 and 3/4 if $\rho = 1/3$ or $\rho = 3$.

A. Two-phase regime

The two-phase regime occurs when $\theta(\mu)$, $\xi(\mu)$, and $\chi(\mu)$ do not reduce to their single-phase values, which is true if both $\lambda_-(\mu)$ and $\lambda_+(\mu)$ are of order larger than N^{-1} [19]. This can hold only near the transition—for

$$\beta|\mu - \mu_t| \leq \delta \quad (9)$$

with a small $\delta > 0$. Indeed, taking the Taylor expansion $\Delta f(\mu) = -\Delta\theta(\mu - \mu_t)[1 + O(\beta|\mu - \mu_t|)]$ of Δf around μ_t , it is required that $\exp(\Delta\theta N\delta)$ is small compared to N . To be specific, we shall take

$$\delta = \frac{3}{4\Delta\theta} \frac{\ln N}{N} \quad (10)$$

(instead of 3/4 any number between 1/2 and 1 can be used); then the order of λ_{\pm} is $N^{-3/4}$ or larger.

Combining Eqs. (4) and (7) with the Taylor expansion

$$f'(\mu) = f'(\mu_t) + \frac{\partial f'(\mu_t)}{\partial\mu}(\mu - \mu_t) + O[\beta^2(\mu - \mu_t)^2] \quad (11)$$

(the prime denotes a derivative with respect to μ or ε_b), within the two-phase interval (9) we get

$$\begin{aligned}\theta(\mu) &= \theta_- \lambda_-(\mu) + \theta_+ \lambda_+(\mu) + O(\delta), \\ \xi(\mu) &= \xi_- \lambda_-(\mu) + \xi_+ \lambda_+(\mu) + O(\delta), \\ \chi(\mu) &= (\Delta\theta)^2 \beta N \lambda_+(\mu) \lambda_-(\mu) [1 + O(1/N^{1/4})],\end{aligned}\tag{12}$$

where ξ_{\pm} are the single-phase average numbers, $\partial f_{\pm}(\mu)/\partial \varepsilon_b$, of occupied bonds per site at μ_t . Note that in the two-phase region (9) the coverage θ ranges within the interval

$$t_- \leq \theta \leq t_+, \tag{13}$$

where $t_{\pm} = \theta(\mu_t \pm \delta) = \theta_{\pm} \mp \Delta\theta \rho^{\pm 1} N^{-3/4} + O(\delta)$. Thus, the coverage attains almost all values from θ_- to θ_+ .

According to Eq. (12), the dependence of θ , ξ , and χ on μ in the two-phase region is primarily given by the weights λ_{\pm} . Evaluating $\lambda_{\pm}(\theta)$ from the relation $\theta(\mu)$ and equality $\lambda_+ + \lambda_- = 1$, we readily obtain the coverage dependences of ξ and χ . Substituting them into Eqs. (1) and (2), we arrive at the result

$$D_c(\theta) \approx \frac{D_c^0 e^{\beta \mu_t}}{\Delta\theta N} \left(\frac{P_-}{\theta - \theta_-} + \frac{P_+}{\theta_+ - \theta} + \epsilon \right) (1 + \epsilon), \tag{14}$$

where $P_{\pm} = 1 - 2\theta_{\pm} + \xi_{\pm}/3$ is the probability of finding a vacant bond in phase p_{\pm} at the transition and the error term $\epsilon = O(N^{3/4}\delta) = O(N^{-1/4} \ln N)$. This result holds only for coverages in interval (13).

Formula (14) shows that in the two-phase regime the coverage dependence $D_c(\theta)$ of the diffusion coefficient decreases with the system size as $1/N$. For a given size, it slowly varies if θ is well between t_- and t_+ , while it increases as the hyperbole $P_{\pm}/\Delta\theta N|\theta - \theta_{\pm}|$ if θ is close to t_{\pm} . If we neglect thermal effects and the error term ϵ , we can approximately write

$$D_c(\theta) \approx \frac{D_c^0 e^{\beta \mu_t}}{N} \times \begin{cases} 3/2\theta & \text{transition } p_0 - p_{2/3}, \\ 3/2(3\theta - 1) & \text{transition } p_{1/3} - p_1, \\ 1/\theta & \text{transition } p_0 - p_1. \end{cases} \tag{15}$$

In Fig. 2 we depict $D_c(\theta)$ in the two-phase interval for four examples of first-order phase transitions chosen as follows.

(T1) Transition $p_0 - p_{2/3}$: $\varepsilon_t > 0$ (repulsion), $\varepsilon_b = -\varepsilon_t/2$ (attraction), and $|\mu - \mu_0| \leq \varepsilon_t$ with $\mu_0 = 3\varepsilon_b/2$.

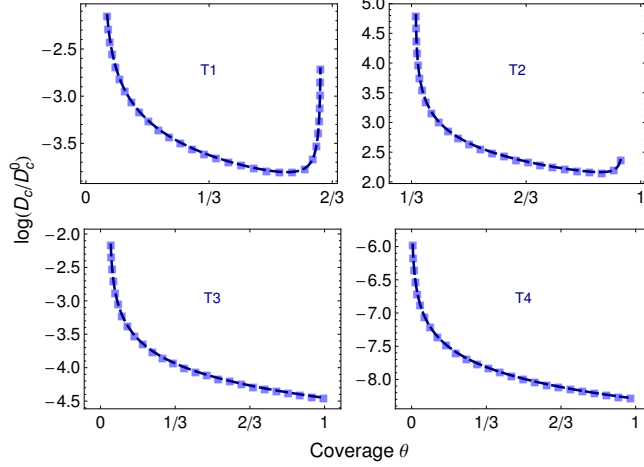


FIG. 2: The coverage dependence of the logarithm the diffusion coefficient D_c (relative to D_c^0) in the two-phase region (13) for $N = 30 \times 40$. The bond interactions are $\varepsilon_b = (-1/2)\varepsilon_t < 0$ for T1, $\varepsilon_b = (-4/3)\varepsilon_t > 0$ for T2, $\varepsilon_b = (-2/5)\varepsilon_t > 0$ for T3, and $\varepsilon_b = (-5/3)\varepsilon_t < 0$ for T4. The triangle interaction $\beta|\varepsilon_t| = 4$ in all cases. Squares correspond to numerical values, whereas dashed lines to formula (14).

(T2) Transition $p_{1/3} - p_1$: $\varepsilon_t < 0$ (attraction), $\varepsilon_b = -4\varepsilon_t/3$ (repulsion), and $|\mu - \mu_0| \leq |\varepsilon_t|$ with $\mu_0 = (9\varepsilon_b + 6\varepsilon_t)/2$.

(T3) Transition $p_0 - p_1$: $\varepsilon_t < 0$ (attraction), $\varepsilon_b = -\varepsilon_t/3$ (repulsion), and $|\mu - \mu_0| \leq |\varepsilon_t|$ with $\mu_0 = 3\varepsilon_b + 2\varepsilon_t$.

(T4) Transition $p_0 - p_1$: $\varepsilon_t > 0$ (repulsion), $\varepsilon_b = -2\varepsilon_t$ (attraction), and $|\mu - \mu_0| \leq \varepsilon_t$ with $\mu_0 = 3\varepsilon_b + 2\varepsilon_t$.

The dependence $D_c(\theta)$ is obtained first numerically from Eqs. (1), (4), and (7) and then compared to values yielded by formula (14) with the error term ϵ neglected (in fact, the logarithm of D_c to base 10 is plotted for better clarity). Obviously, the analytical formula very accurately reproduces the numerical results.

B. Crossover regimes

At either end the two-phase region is neighbored by a crossover region in which $\theta(\mu)$, $\xi(\mu)$, and $\chi(\mu)$ rapidly reduce from two-phase to single-phase values. This corresponds to a

decrease in the order of either $\lambda_-(\mu)$ or $\lambda_+(\mu)$ from above N^{-1} below it. The two crossovers take place within the regions

$$\delta \leq \beta|\mu - \mu_t| \leq d, \quad d = \frac{5}{4\Delta\theta} \frac{\ln N}{N}, \quad (16)$$

in which the order of λ_{\pm} reduces from $N^{-3/4}$ to $N^{-5/4}$. Using the upper (lower) signs for the crossover above (below) μ_t , from Eqs. (4) and (7) we get

$$\begin{aligned} \theta(\mu) &= \theta_{\pm} \pm \chi_{\pm}|\mu - \mu_t| \mp \Delta\theta\rho^{\pm 1}e^{-\Delta\theta\beta N|\mu - \mu_t|} + \epsilon, \\ \xi(\mu) &= \xi_{\pm} \pm \zeta_{\pm}|\mu - \mu_t| \mp \Delta\xi\rho^{\pm 1}e^{-\Delta\theta\beta N|\mu - \mu_t|} + \epsilon, \\ \chi(\mu) &= \chi_{\pm} + (\Delta\theta)^2\beta N\rho^{\pm 1}e^{-\Delta\theta\beta N|\mu - \mu_t|} + \beta N\epsilon, \end{aligned} \quad (17)$$

where $\zeta_{\pm} = (\partial^2 f_{\pm}/\partial\mu\partial\varepsilon_b)_{\mu_t}$, χ_{\pm} are the single-phase susceptibilities, $-\partial^2 f_{\pm}(\mu)/\partial\mu^2$, at the transition, and the error $\epsilon = O(N^{-3/2})$. Thus, in the crossovers the coverage ranges within the intervals

$$\tau_- \leq \theta \leq t_-, \quad t_+ \leq \theta \leq \tau_+ \quad (18)$$

with $\tau_{\pm} = \theta(\mu_t \pm d) = \theta_{\pm} \pm (\chi_{\pm}/\beta)d + O(N^{-5/4})$. Intervals (18) are very narrow and concentrated around θ_{\pm} .

The μ dependences of θ , ξ , and χ in Eq. (17) are essentially only via $|\mu - \mu_t|$. Evaluating the latter [or, more conveniently, evaluating $\exp(-\Delta\theta\beta|\mu - \mu_t|N)$ as a function of θ , the coverage dependences of ξ and χ can be deduced. Combining them with Eqs. (1) and (2), we get

$$D_c(\theta) \approx D_c^0 e^{\beta\mu_t} \frac{P_{\pm} + \frac{P'_{\pm}}{\chi_{\pm}}(\theta - \theta_{\pm}) \pm \left(\frac{P'_{\pm}}{\chi_{\pm}} - \frac{\Delta P}{\Delta\theta}\right) \frac{\omega_{\pm}(\theta)}{C_{\pm}} + \epsilon}{\frac{1}{\beta}\chi_{\pm}[1 + \omega_{\pm}(\theta)](1 + N\epsilon)} \quad (19)$$

with

$$\omega_{\pm}(\theta) = W(\Delta\theta\rho^{\pm 1}C_{\pm}e^{\mp C_{\pm}(\theta - \theta_{\pm})}), \quad (20)$$

where $P'_{\pm} = -2\chi_{\pm} + \zeta_{\pm}/3$ represents the rate of change of P with μ in a given phase at the transition, the shorthand $C_{\pm} = \Delta\theta\beta N/\chi_{\pm}$, and $W(y)$ is the Lambert function (the inverse to $y = W \exp W$). The upper (lower) signs in formula (19) correspond to the crossover around θ_+ (θ_-).

If θ is near the two-phase region (close to t_{\pm}), then $\omega_{\pm} \approx C_{\pm}|\theta - \theta_{\pm}| \gg 1$ so that $D_c(\theta)$ still increases as the two-phase hyperbole $P_{\pm}/\Delta\theta N|\theta - \theta_{\pm}|$. On the other hand, if θ is distant from

the two-phase region (close to τ_{\pm}), then $\omega_{\pm} \approx \Delta\theta\rho^{\pm 1}C_{\pm}\exp(-C_{\pm}|\theta - \theta_{\pm}|) \ll 1$ so that the diffusion coefficient behaves as $[P_{\pm} + (P'_{\pm}/\chi_{\pm})(\theta - \theta_{\pm})]/(\chi_{\pm}/\beta)$, i.e., it is linearly disturbed from the constant value $P_{\pm}/(\chi_{\pm}/\beta)$. Thus, within a crossover region the diffusion coefficient suddenly changes from the hyperbolic increase to a slight linear increase (or decrease) as θ moves from two-phase region across θ_{\pm} towards a single-phase region. The dependence $D_c(\theta)$ in the crossover regions for transitions T1 – T4 is shown in Fig. 3.

C. Single-phase regimes

Finally, far from the transition there is a single dominant phase: p_- for μ below $\mu_t - d$ (or, θ below τ_-) and p_+ for μ above $\mu_t + d$ (or, θ above τ_+). Then $\theta(\mu)$, $\xi(\mu)$, and $\chi(\mu)$ reduce to their single-phase values. Indeed, denoting p_{α} the stable phase, Eqs. (4) and (7) yield

$$\begin{aligned}\theta(\mu) &= -\frac{\partial f_{\alpha}(\mu)}{\partial \mu} + O(N^{-5/4}), \\ \xi(\mu) &= \frac{\partial f_{\alpha}(\mu)}{\partial \varepsilon_b} + O(N^{-5/4}), \\ \chi(\mu) &= -\frac{\partial^2 f_{\alpha}(\mu)}{\partial \mu^2} + O(\beta N^{-5/4}).\end{aligned}\tag{21}$$

The coverage dependence of D_c in this regime follows by obtaining the inverse to $\theta(\mu)$, using expression (5) for f_{α} . This is simple for $\alpha = 0, 1$, while for $\alpha = 1/3, 2/3$ we may take into account that $\ln(1+x) \approx x$ because $x \sim \exp(-\text{const } \beta)$ is small. We get the approximative formulas

$$\frac{D_c}{D_c^0} \approx \begin{cases} (1-2\theta)/(1-\theta)^2 & \text{regime of } p_0, \\ (5-9\theta+a)(3\theta-1+a)/8q_b^3a & \text{regime of } p_{1/3}, \\ 2/q_b^3\sqrt{8q_b^3q_t^6+(2-3\theta)^2} & \text{regime of } p_{2/3}, \end{cases}\tag{22a}$$

and $D_c \approx 0$ in the regime of phase p_1 , where $a = [8q_b^3 + (1-3\theta)^2]^{1/2}$ and $q_b = \exp(-\beta\varepsilon_b)$. Since for phase p_1 the approximation of f_1 that uses only one-site perturbations is not sufficient to get a non-vanishing $D_c(\theta)$, we need to take into account the next dominant contributions arising from two-site perturbations (the removal of two particles in a bond). Then an additional term $(-3/\beta)\ln[1 + \exp(-\beta\Delta H_1^{\bullet\bullet})]$ appears in f_1 , where $\Delta H_1^{\bullet\bullet} = 2\mu - 11\varepsilon_b - 10\varepsilon_t$ is the energy excess of a two-site perturbation of σ_1 over the energy of σ_1 . Applying this

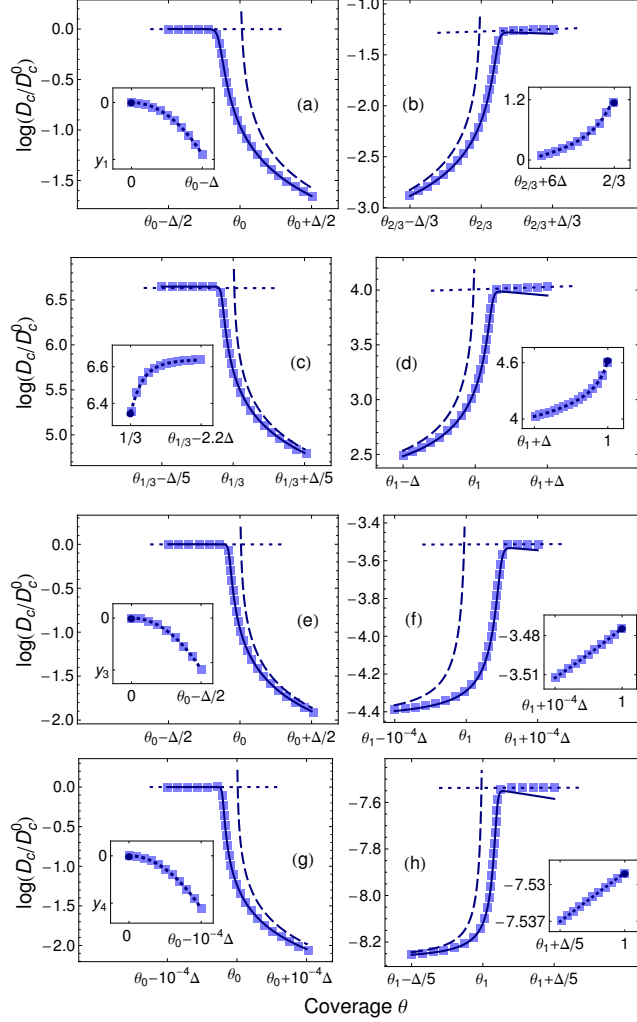


FIG. 3: The coverage dependence of the logarithm of the diffusion coefficient (relative to D_c^0) in the crossover and single-phase regions for the same system size and interparticle interactions as in Fig. 2. Squares represent numerical values, whereas dashed and solid lines formula (14) and (19), respectively. Dotted lines represent the analytical dependence obtained in the single-phase regions, while disks the limiting values. The values $\Delta = N^{-3/4}$, $y_1 = -1 \times 10^{-3}$, $y_3 = -7 \times 10^{-4}$, and $y_4 = 1.2 \times 10^{-11}$.

refined expression for f_1 , we get

$$D_c(\theta) \approx \frac{D_c^0}{q_b^5 q_t^4 \sqrt{1 + 24 q_b q_t^2 (1 - \theta)}} \quad \text{regime of phase } p_1 \quad (22b)$$

with $q_t = \exp(-\beta \varepsilon_t)$.

The dependence $D_c(\theta)$ in the single-phase regions for transitions T1 – T4 is detailed in the insets in Fig. 3. It turns out that $D_c(\theta)$ does not diverge (as might be incorrectly

conjectured from the behavior of D_c in the two-phase and crossover regions) but tends to the constant values 1, $(1 + \sqrt{2q_b^3})/4q_b^3$, $1/\sqrt{2q_b^9 q_t^3}$, and $1/q_b^5 q_t^4$ as θ approaches 0, $1/3$, $2/3$, and 1, respectively. However, the model does not allow us to analyze the behavior of $D_c(\theta)$ on both sides of $\theta = 1/3, 2/3$ (due to the infinite number of ground states on the lines separating the regions of ground states $\sigma_0, \sigma_{1/3}$ and $\sigma_{2/3}, \sigma_1$).

IV. CONCLUDING REMARKS

Figure 3 demonstrates how one analytical approximation quite smoothly takes over from another one as the coverage gets from one of the three regions to another. It turns out that the agreement increases rather fast with the system size N .

Although the coverage dependence of D_c in the single-phase region as approximated by Eq. (22) is model dependent, the two-phase and crossover regions formulas (14) and (19) are actually true for the general case of a first-order phase transition between two phases at low temperatures. Indeed, in the local equilibrium limit D_c can be approximated by Eq. (1) in which the factor P is a sum of the probabilities that two or more neighboring lattice sites are occupied by adparticles [6, 16, 17]. Thus, rather generally, one has $P = a_0 + \sum_i a_i (\partial f / \partial p_i)$, where a_i are constants and p_i are suitable parameters (such as the chemical potential or interparticle interactions). Hence, formulas (14) and (19) can be readily extended to this general form of P by setting $P_{\pm} = a_0 + \sum_i a_i (\partial f_{\pm} / \partial p_i)_{\mu_t}$ and $P'_{\pm} = \sum_i a_i (\partial^2 f_{\pm} / \partial \mu \partial p_i)_{\mu_t}$. The physical meaning of these quantities remains the same: P_{\pm} are the single-phase values of P and P'_{\pm} is the rate of change of P with μ in a given phase, both evaluated at the transition.

Finally, note that Eq. (14) can yield the Langmuir relation, $D_c(\theta) = \text{const} / (1 - \theta)$, if phase p_+ is fully occupied, its factor P_+ is strictly positive, and the factor P_- in the other phase is negligible. This is not the case for the form of P given by Eq. (2).

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